A Simple Equation of State for Associating Fluids

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A relatively simple equation of state for associating fluids is proposed. This equation takes cubic Soae-Redlich-Kwong (SRK) equation of state as a frame for representing the physical part in interaction of fluid molecules and it incorporates an associating term that is used for the chemical part. The associating term comes from the bonding term of statistical associating fluid theory (SAFT) in which the fluid molecules are considered to form only dimers. The resulting equation of state contains four adjustable parameters, among which three parameters are the inherent variables of SRK equation and another one is regarded as association mole fraction. The parameters are determined using vapor pressures and saturated liquid densities of pure associating fluids. The excellent correlation of both vapor pressure and saturated liquid volume are obtained for 37 pure associating fluids such as alcohols, carboxylic acids, amines and water. The total average absolute deviations between the calculated values and experimental data are 0.09% in vapor pressure and 0.48% in saturated liquid volume respectively. The estimated pure compound parameters have been tested in prediction of second virial coefficients with satisfactory results. The calculated results are also compared with those given by SAFT and CPA (Cubic Plus Association) equation and show that this equation is more simple and reliable than SAFT and CPA equations for engineering application.

KEY WORDS: model; association fluid; perturbation theory; SAFT.

1. INTRODUCTION

Equations of state are used in engineering practice to predict the thermodynamic properties of fluids. However, cubic equations of state are the most frequently used equations of state for practical applications due to the fact that they offer the best balance between accuracy, reliability, simplicity and speed of computation. But cubic equations of state, such as SRK EOS[1] and PR EOS[2] are failed in predicting the thermophysical properties and phase equilibria for associating fluids. It is well known that species forming hydrogen bonds often exhibit unusual thermodynamic behavior.

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The strong attractive interaction between molecules results in the formation of molecular clusters. Thus, the chemical equilibria between associating molecules should be taken into account in order to develop a reliable thermodynamic model.

Recently, a number of associating EOS have been proposed. Chemical theory has been shown by many authors to be useful for treating associating fluids. Heidemann and Prausnitz[3] applied the chemical theory to yield an equation of state that can be very accurate for the calculation of PVT properties of pure fluids. This has been demonstrated by Twu et al.[4,5], who applied this method in conjunction with the Redlich-Kwong EOS to carboxylic acids and hydrogen fluoride. Ikonomou and Donohue[6] used the concept of Heidemann and Prausnitz in conjunction with the PACT equation of state. Anderko[7,8] also developed an equation for associated mixtures that combines a cubic EOS with a chemical term that accounts for association. Except for the Chemical theory, lattice/quasi-chemical theory is also used by Panayiotou and Sanchez[9], they postulated the separation of the partition function into 'physical' and 'chemical' parts. The first part is treated with a lattice-fluid equation, and the second one with an approach similar in spirit to that of the quasi-chemical theory. From this modern point of view, a more promising route for understanding the properties of associating fluids is provided firmly based on statistical mechanics. Chapman et al. [10,11] recently reported an equation of state based on the Statistical Associating Fluid Theory(SAFT). Huang and Radosz [12,13] have applied the SAFT to a variety of real fluids including polymers. The reference part of SAFT includes the hard sphere, chain and association terms. The perturbation part accounts for relatively weaker, mean-field(e.g., dispersion)effects.

The three different categories of developed models above for associating fluids is theoretically sound, but they still are not convenient for engineering application. Peschel and Wenzel[14] showed that whatever expression is used for the physical part(a cubic or a noncubic equation of state), the resulting models yield similar results. Thus, Kontogeorgis[15]et al. incorporated an association term similar to that used in the SAFT into the framework of the SRK equation of state. In this work, we supposed that the molecules of associating fluids only form partly dimer due to self-association for pure component. It is different from CPA equation, we incorporated the expression of dimer which is derived from chain term of SAFT into the framework of SRK equation. The resulting equation is more simple than the CPA equation of state, and superior to SAFT

equation in the calculation accuracy for pure associating fluids.

2. EQUATION OF STATE

In the SAFT, the compressibility factor of chain fluids can be presented as

$$Z = 1 + Z^{seg} + Z^{chain} + Z^{assoc} \tag{1}$$

where Z^{seg}, Z^{chain} and Z^{assoc} are the compressibility factors of segment, chain contribution and association contribution, respectively. In equation(1), association term is the summation over all association sites,

$$Z^{assoc} = \rho \sum_A \left[\frac{1}{X^A} - \frac{1}{2} \right] \frac{\partial X^A}{\partial \rho} \tag{2}$$

As pointed out by Huang and Radosz[12], the association schemes of real fluids depend on the associating compound. For example, carboxylic acids are known to form stable dimers, thus the monomer-dimer model of chemical theory should be used. Alcohols as well as a variety of compounds, e.g., phenol, amines, pyridine base etc. are known, through independent spectroscopic measurements, to form also dimers and higher oligomers(e.g. trimers, tetramers, etc.) besides dimers.

Eq.(2) describes well the association contribution, but Z^{assoc} is not easy to be evaluated, which needs five microscopic segment parameters[12]: v^{00}, temperature-independent segment volume; m, effective number of segments within a molecule; u^0/k, temperature-independent dispersion energy of interaction between segments; ε/k, association energy of interaction between sites A and B and k, volume of interaction between sites A and B. If we combine directly a cubic equation of state with the association term of SAFT, it would lead to a complicated multi-parameter equation which contains a mixture of molecular parameters (a and b) and segment parameters (v^{00}, m, u^0/k, ε/k, and k).

However, our purpose is to develop a relatively simple equation of state with theoretical basis. We found that in SAFT equation(1), the chain term is derived based on the associating fluid theory, where the associated bonds are replaced by covalent, chain-forming bonds based on Chepman[16] and Chapman et al.[17]. Therefore for the reason of simplicity, we assumed that the dimerization takes place only in the associating fluids due to self association, e.g. the associated species possible are only dimers. We decided to describe the dimerization utilizing the chain term rather than

association term. The compressibility factor of chain contribution for pure component is given blow

$$Z^{chain} = (1-m)\rho \left[\frac{\partial \ln g(d)^{hs}}{\partial \rho} \right]_T \tag{3}$$

The hard sphere radial distribution function is presented by Carnahan and Starling[18]

$$g^{hs}(d) = \frac{2-\eta}{2(1-\eta)^3} \tag{4}$$

where

$$\eta = \frac{b}{4V}$$

Eq.(4) is substituted into eq.(3), the result is obtained as follows

$$Z^{chain} = (1-m)\frac{5\eta - 2\eta^2}{(1-\eta)(2-\eta)} \tag{5}$$

Let m=2, then

$$Z^{chain} = Z^{dimer} = -\frac{5\eta - 2\eta^2}{(1-\eta)(1-\eta)} = -\frac{2b(10V-b)}{(4V-b)(8V-b)} \tag{6}$$

While SRK equation of state incorporates the equation(6), finally, a relatively simple equation of state for pure compound is given below

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} - \frac{2\beta RT(10V-b)}{(4V-b)(8V-b)} \tag{7}$$

Equation(7) takes SRK equation of state as a frame for representing the physical part in interaction of fluid molecules, and the association term with the theoretical background is employed for the chemical part. This equation is not cubic with respect to volume. The parameter a is from the physical part of eq.(7) and the covolume parameter b apperars in both the physical and the association part. The parameter β is an experiential one which is introduced into eq.(7)to be referred to as an associating factor, that reflects the fact that there exists a chemical equilibrium between the monomer and dimer in the association fluids.

3. RESULTS AND DISCUSSION

The new equation of state for pure associating fluid as described above contains the parameter a related to attraction energy, van der Waals's covolume b, and the associating factor β. The energy parameter a is treated as a temperature-dependency one analogizing to Soave-type formula

$$a = a_0 \left(1 + c_1 \left(1 - \sqrt{T_r}\right)\right)^2 \tag{8}$$

The covolume parameter b is assumed to be temperature-independent, in agreement with most published equation of state. The parameter β is an associating factor which represents the association extent of each compound. It is evident that, for nonassociating substances, $\beta = 0$, and the eq.(7)is reduced to SRK equation. In principle, adjustable parameter β is related to temperature. But the test of calculation value of β for all kinds of associating compound demonstrated that β is approximately a temperature-independence constant in a broad range of temperature except for the neighborhood of critical point. Fig.1 showed the change of association factor β with temperature for water. It is seen from Fig.1 that the change of β value is below 5% within temperature range from T_r=0.55 to T_r=0.90. This is the reason why association factor β is taken as a constant of temperature-independence for each associating compound.

Therefore, the new equation of state for pure associating fluid contains four adjustable parameters(a_0, c_1, b and β) which are determined using vapor pressures and saturated liquid densities of pure component. All experimental data for vapor pressures and liquid densities have been taken from the DIPPR data compilation[19]. The optimization is based on both vapor pressures and saturated liquid densities. The objective function which has been used is the following

$$F_{obj} = \sum_{i=1}^{N} \left[\left(\frac{p_i^{cal} - p_i^{exp}}{p_i^{exp}} \right)^2 + \left(\frac{V_i^{cal} - V_i^{exp}}{V_i^{exp}} \right)^2 \right] \tag{9}$$

For each associating compound, Table 1 lists the temperature range, four parameters b, a_0, c, β and $\Delta P\%$ in vapor pressure between the calculated values and experimental data, $\Delta V\%$ in liquid volume between the calculated results and experimental data using the new equation of state and SAFT equation respectively. It is

seen from Table 1 that the excellent correlation of both vapor pressure and liquid volume with the new equation of state are obtained for 37 pure associating fluids including alcohols, carboxylic acids, amines and water. The total average absolute deviations for all pure associating substances between the calculated values and experimental data are 0.09% in vapor pressure and 0.48% in the saturated liquid volume respectively. The calculated results also show that the simple equation of state can give more satisfactory results than SAFT equation for pure associating compounds.

The literature[15]only provided the correlation results with CPA equation for various alcohols. Thus we also compared the calculated vapor pressures with the new equation and CPA equation in Table 2. The comparison demonstrated that the new equation can get more accurate results than CPA equation.

The magnitude of parameters a_0, and b increases with increasing carbon number within each homologous series practically linearly. For example, a_0 and b for normal alcohols are plotted versus carbon number in Figs. 2 and 3. For the case of estimating, a_0 and b have been regressed as a simple linear function of carbon number c_n for the various homologous series,

for alcohols

$$a_0 = 0.125 + 0.490 \times c_n$$
$$b = 1.454 \times 10^{-5} + 1.686 \times 10^{-5} \times c_n$$

for carboxylic acids

$$a_0 = 0.225 + 0.552 \times c_n$$
$$b = 2.042 \times 10^{-5} + 1.524 \times 10^{-5} \times c_n$$

for amines

$$a_0 = 0.228 + 0.581 \times c_n$$
$$b = 1.791 \times 10^{-5} + 1.678 \times 10^{-5} \times c_n$$

It is well know that the prediction for second virial coefficients through an equation of state is a very strict test of its performance, cubic equations of state do not predict second virial coeffiient accurately, especially at low temperatures[15]. In order to test the ability of the new equation, the second virial coefficients of normal alcohols are predicted in this study using the new equation with the parameters listed in Table 1. Fig.4 represented the satisfactory agreement between the predicted values and experimental datafor methanol[20]. The result described above demonstrated that the new simple equation of state has very good performance in the calculation of

thermodynamical properties for pure associating fluids.

4. CONCLUSIONS

A new simple equation of state for associating compounds proposed by us combines the simplicity of SRK equation of state with the chain term of SAFT equation based on perturbation theory. The resulting equation of state can provide an excellent correlation of both vapor pressure and saturated liquid volume of associating fluids with four temperature-independence parameters. The prediction of the second virial coefficients of normal alcohols also represents very good performance of the new equation. Our future work will extend the new simple equation to mixtures, especially phase equilibria.

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Table I. Correlation Results of Vapor Pressure and Saturated Liquid Volume

compound	T (K)	b $\times 10^5$	a_0	c_1	β	New EOS		SAFT	
						$\triangle P(\%)$	$\triangle V(\%)$	$\triangle P(\%)$	$\triangle V(\%)$
Water	356-582	1.4974	0.4373	0.3621	0.0944	0.04	0.58	1.30	3.20
Methaanol	282-461	3.4853	0.8235	1.0476	0.0086	0.13	0.26	0.83	0.88
Ethonal	284-465	5.1972	1.1953	1.5833	0.0870	0.19	0.43	0.86	0.83
1-Propanol	292-483	6.9364	1.5874	2.1964	0.1090	0.22	0.69	0.16	1.20
2-Propanol	280-457	6.7638	1.5332	1.4836	0.0735	0.18	0.42	0.27	0.96
1-Butanol	310-507	7.1843	1.7843	0.0617	0.1991	0.02	0.34	0.23	1.00
sec-Butanol	292-482	8.3234	1.8699	1.7223	0.1105	0.16	0.60	0.32	1.20
tert-Butanol	278-456	8.2897	1.7917	1.5286	0.0197	0.15	0.64	-	-
iso-Butanol	301-492	8.5171	2.0225	1.8231	0.2219	0.22	0.45	-	-
1-Pentanol	322-528	9.8750	2.5552	1.3389	0.0906	0.16	0.38	0.32	1.10
2-Pentanol	304-497	9.8679	2.3316	1.4966	0.0052	0.18	0.65	-	-
3-Pentanol	301-492	9.7888	2.2691	1.7058	0.0051	0.19	0.78	-	-
1-Hexanol	336-550	10.872	2.7768	0.0087	0.3261	0.01	0.33	0.77	1.22
1-Heptanol	348-569	13.172	3.5722	1.2865	0.0930	0.11	0.49	0.61	0.96
1-Octanol	359-587	14.986	4.2273	1.4037	0.0022	0.12	0.62	1.00	1.00
1-Nonanol	370-606	16.569	4.6626	1.3124	0.0022	0.14	0.47	1.10	0.47
1-Decanol	380-621	18.962	5.0222	0.0874	0.0019	0.02	0.08	2.10	0.57
Methanoic	319-522	3.1440	0.8724	0.8092	0.0081	0.04	0.23	0.62	0.49
Ethanoic	326-533	5.0415	1.3443	0.7696	0.0054	0.04	0.24	1.60	0.69
n-Propanoic	337-551	6.8452	1.8239	1.0931	0.0094	0.05	0.54	0.25	0.10
n-Butanoic	342-565	9.3510	2.5942	1.2781	0.0092	0.11	0.60	0.30	0.84
n-Pentanoic	358-586	10.325	2.8942	1.3882	0.0093	0.11	0.60	0.21	1.00
n-Hexanoic	367-600	11.817	3.4517	1.1871	0.0074	0.16	0.46	0.44	-
n-Heptanoic	374-612	13.523	3.9194	1.1729	0.0073	0.12	0.67	0.46	-
n-Octanoic	381-623	15.175	4.6247	1.3460	0.0093	0.22	0.59	0.60	-
n-Nonanoic	387-633	16.870	4.9951	1.2247	0.0090	0.17	0.77	0.44	-
n-Decanoic	392-642	18.792	6.0941	1.2496	0.0072	0.26	0.82	0.60	-
Methylamine	237-387	3.5831	0.6462	0.7597	0.0088	0.02	0.17	0.22	0.38
Ethylamine	251-411	5.1960	1.0287	0.7196	0.0089	0.01	0.28	0.27	0.22
n-Propylamine	273-447	6.8028	1.4889	0.7903	0.0094	0.02	0.19	1.30	1.50
n-Butylamine	293-479	8.3976	1.9737	0.8701	0.0277	0.02	0.18	2.20	2.60
n-Pentylamine	302-500	10.317	2.5006	1.3665	0.0096	0.11	0.59	2.30	2.00
n-Hexylamine	321-525	11.779	3.0504	0.9721	0.0084	0.04	0.27	0.84	1.70
n-Heptylamine	334-546	13.274	3.5600	0.8657	0.0078	0.04	0.33	1.50	0.99
n-Octylamine	342-564	15.175	4.6247	1.3460	0.0093	0.22	0.59	-	-
n-Nonylamine	356-583	16.936	4.7328	1.1025	0.0089	0.06	0.54	-	-
n-Decylamine	362-597	18.792	6.0410	1.2496	0.0072	0.26	0.82	-	-

Table II．Comparison of The Correlation Results for Vapor Pressure

of Normal Alcohols with New EOS and CPA

| compound	$\triangle P(\%)$	
	New EOS	CPA
Methaanol	0.13	0.33
Ethonal	0.19	0.17
1-Propanol	0.22	0.39
1-Butanol	0.02	0.31
1-Pentanol	0.16	0.32
1-Hexanol	0.01	0.18
1-Octanol	0.12	0.33
1-Nonanol	0.14	0.52

Captions

1. Fig. 1   The change of association factor β with temperature for water.

2. Fig. 2   Parameter a_0 as the linear function of carbon number c_n for normal alcohols.

3. Fig. 3   Parameter b as the linear function of carbon number c_n for normal alcohols.

4. Fig. 4   Prediction of second virial coefficients for methanol.

   $\triangle$,   experimental data;   ——— ,   predicted values by new EOS;

   ············· ,   predicted values by SRK.
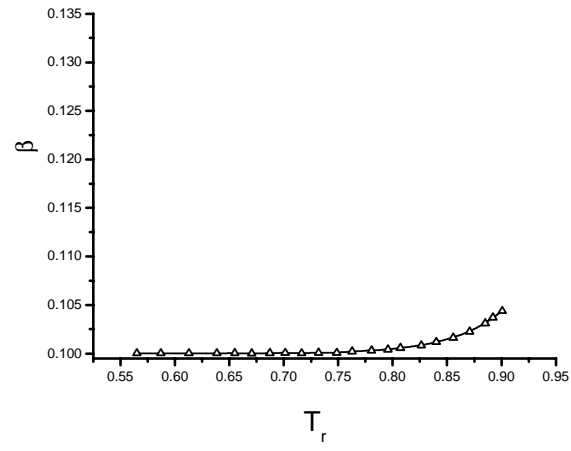
Fig.1   The change of association factor β with temperature for water.
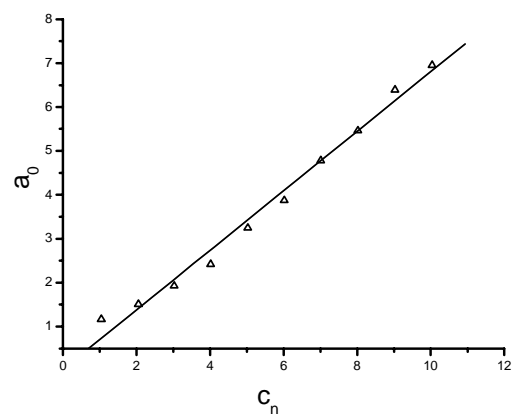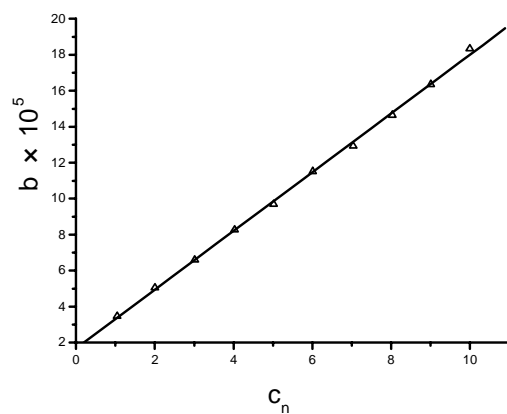
Fig.2　Parameter a_0 as the linear function of carbon number c_n for normal alcohols.

Fig.3   Parameter b as the linear function of carbon
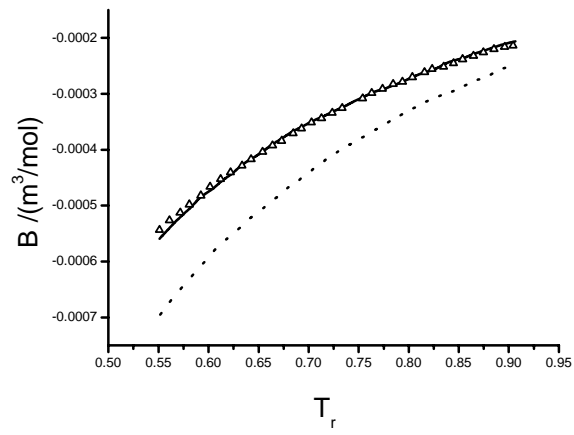number c_n for normal alcohols.

Fig. 4   Prediction of second virial coefficients for methanol.
△,   experimental data; ——— ,   predicted values by new EOS;
·············· ,   predicted values by SRK.